9"

To be published in JVST (Proceedings of PCSI-20)

Novel Si-based superlattices consisting of alternating layers of crystalline Si and porous amorphous $Si_{1-x}Ge_x$ alloys

R.W. Fathauer, T. George, E.W. Jones, W.T. Pike, A. Ksendzov, and R.P. Vasquez

Center for Space Microelectronics Technology, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

ABSTRACT

Superlattices consisting of alternating layers of crystalline Si and porous amorphous $Si_{1-x}Ge_x$ have been studied. These are fabricated by immersing mesa structures of molecular-beam-epitaxy grown $Si/Si_{0.7}Ge_{0.3}$ superlattices in an $HF:HNO_3:H_2O$ solution. A high selectivity in the pore formation leads to lateral penetration of pores ≈ 0.7 µm into 5-nm-thick $Si_{0.7}Ge_{0.3}$ layers. The effect of the etch on layers with differing alloy composition, thickness, and strain has been examined. Homogeneous strain has been identified as an important factor in establishing the selectivity of the etch, but other factors clearly play important roles as well.

The ability to synthesize Si-based materials with new optical, photonic, and electronic properties is greatly desired. Despite considerable effort, Si-based superlattices demonstrated to date have exhibited limited new properties,[1,2] suggesting that new classes of structures may be required. In addition, $Si/Si_{1-x}Ge_x$ heterojunctions are limited by a small conduction-band discontinuity and large lattice mismatch.[2] We have recently fabricated novel superlattices consisting of alternating layers of crystalline Si and porous amorphous $Si_{1-x}Ge_x$.[3] Conversion of the porous layers in such structures to oxides or other materials may also allow additional superlattices and novel heterojunction systems with large band offsets to be realized.

Recent reports of visible light emission from porous Si[4] have stimulated renewed interest in this material. Porous Si is most commonly formed by electrochemical etching of Si in aqueous HF, resulting in thick porous Si layers on Si substrates. However, simple immersion of Si wafers in "stain etches" such as $HF:HNO_3:H_2O$, also yields light-emitting porous Si.[5,6] In contrast to many of the reports on electrochemically -produced porous Si, these films are predominantly amorphous.[5,7,8]

$Si/Si_{1-x}Ge_x$ structures were grown at 500-550°C on two-inch diameter 1-3 Ω-cm n-type (loO)-oriented Si wafers, The substrates were chemically cleaned *ex situ*, leaving a protective oxide which was removed with an HF:ethanol solution in a dry-nitrogen glove box, A Riber EVA 320 molecular beam epitaxy (MBE) system was used for the growth, in which Si and Ge are evaporated from separate electron- beam sources. Fabrication of super] attices consisting of alternating layers of crystalline Si and porous amorphous $Si_{1-x}Ge_x$ was carried out by patterning Al lines, Ar-ion milling to form mesa structures, stripping the Al, and finally by immersion in a stain etch consisting of $HF:HNO_3:H_2O$ in a 4:1:4 ratio by volume. Analysis of these structures was primarily carried out by transmission electron microscopy (TEM) of cross-sectional specimens in a Topcon O02B microscope. Conventional mechanical thinning and ion milling techniques were employed for specimen preparation.

A high selectivity is observed for etching of pseudomorphically-strained $Si_{1-x}Ge_x$ relative to Si, resulting in lateral penetration of the pores to a depth of ≈ ().7 μm in alloy layers flanked by unetched Si layers. Additional etching results in excessive porosification of the Si layers. Superlattices have been fabricated from 1-yin-wide mesas with ten 5-nm-thick $Si_{0.7}Ge_{0.3}$ layers fully converted to ≈ 6-rim-thick porous amorphous layers.[3] A portion of such a superlattice is shown in Fig. 1.

In order to learn more about the selectivity of the etch, several other samples have been examined. One of these contains $Si_{0.7}Ge_{0.3}$ layers with varying alloy layer thicknesses. The penetration depth in a 20-nm-thick layer was found to be several times that in 2.5- or 1-nm-thick layers.[3] This is presumably due to the difficulty of transporting reactants through a very thin channel. The Ge content x has also been varied from 0.2 to ().4 in a sample with 5-nm-thick $Si_{1-x}Ge_x$ layers spaced by 100-nm-thick Si layers. In this sample, lateral penetration of pores is found to increase with increasing x.

In addition to multilayer samples, thick alloy layers with varying Ge content have been examined. For layers above the critical thickness for introduction of misfit dislocations, pores are found to penetrate much further into the layer at threading dislocations, as seen in Fig. 2. Finally, a sample was grown with a relaxed $Si_{0.7}Ge_{0.3}$ buffer layer, on which strained Si layers and relaxed $Si_{0.7}Ge_{0.3}$ layers were grown. Pores again penetrate more deeply at dislocations, but the porous regions stop abruptly at the first strained Si layer, as seen in Fig. 3.

In aqueous solutions with much greater concentrations of HF than HNO_3, etching of Si is expected to be limited by the rate of oxidation. $Si_{1-x}Ge_x$ layers have been observed to oxidize more rapidly than Si,[9] which may partially explain the high selectivity observed for the alloy layers. Oxidation of $Si_{1-x}Ge_x$ layers is known to result in the formation of SiO_2 with Ge enrichment at the interface with the oxide. By examining thick layers etched in the same manner, we have found that the composition of the porous alloy is significantly more Ge rich than the dense alloy.[10] X-ray photoelectron spectroscopy data indicate that the material remaining after etching is more than 90% Ge, demonstrating that Si is removed preferentially during the etching process.

It is also clear that homogeneous strain (due to the lattice mismatch between Si and $Si_{1-x}Ge_x$) plays an important role in establishing the selectivity of the etch. This was demonstrated previously,[3] and is suggested by the enhanced porosification at threading dislocations (though preferential attack of the dislocation core could also account for this). This could also explain the enhanced etching of layers with higher Ge content, which are more heavily strained. However, the chemical content (richer in Ge) of the layers could also account for the enhanced attack. The sample with strained Si layers and relaxed $Si_{1-x}Ge_x$ layers demonstrates that homogeneous strain is not the overriding factor controlling selectivity, though, or the Si would have etched preferentially. There could be a difference in etching as a function of the sign of the strain, though the fact that the strain is biaxial makes a strong effect of this sort seem unlikely. Inhomogeneous strain due to local distortion of bond lengths in the alloy layers may play an important role as well.

For very thin layers, reduced pore formation suggests that transport of reactants and products **can** limit the etching process. Finally, electrochemical effects on the anodic oxidation rate may play an important role. For example, the built-in electric field at heterojunctions and the local distribution of holes could affect pore formation. This could be affected by layer thicknesses, alloy content, layer and substrate doping, and strain.

In summary, superlattices consisting of alternating layers of crystalline Si and porous amorphous $Si_{1-x}Ge_x$ have been studied. These are fabricated by immersing mesa structures of epitaxial $Si/Si_{0.7}Ge_{0.3}$ superlattices in stain etches. The effect of the etch on layers with differing alloy composition, thickness, and strain has been examined. Homogeneous strain has been identified as an important factor in establishing the selectivity of the etch, but other factors clearly play important roles as well.

The work described here was performed by the Center for Space Microelectronics Technology, Jet Propulsion Laboratory, California Institute of Technology. and was sponsored by the Strategic Defense Initiative Organization / Innovative Science and Technology Office through an agreement with the National Aeronautics and Space Administration.

REFERENCES

[1]T.P. Pearsall, Materials Sci. and Eng. B 9,225 (1991).

[2]J.C. Bean, in Silicon Molecular Beam Epitaxy, Vol. II, ed. by E. Kasper and J.C. Bean (CRC Press, Boca Raton, Florida, 1988), Chap. 11.

[3]R.W. Fathauer, T. George, E.W. Jones, W.T. Pike, A. Ksendzov, and R.P. Vasquez, Appl. Phys. Lett. 61,2350 (1992).

[4]L.T. Canham, Appl. Phys. Lett. 57, 1046 (1990), "

[5]R.W. Fathauer, To George, A. Ksendzov, and R.P. Vasquez, Appl. Phys. Lett. 60,995 *(1992).*

[6]S. Shih, K.H. Jung, T.Y. Hsieh, J. Sarathy, J.C. Campbell, and D.L. Kwong, Appl. Phys. Lett. *60, 1863 (1992).*

[7]R.P. Vasquez, R.W. Fathauer, T. George, A. Ksendzov, and T.L. Lin, Appl. Phys. Lett. 60, 1004 (1992).

8T. George, M.S. Anderson, W.T. Pike, T.L. Lin, R. W. Fathauer, K.H. Jung, arid D.L. Kwong, Appl. Phys. Lett. 60,2359 (1992).

[9]F.K. Legoues, R. Rosenberg, T. Nguyen, F. Himpsel, and B.S. Meyerson, J. Appl. Phys. *65,* 1724 (1989).

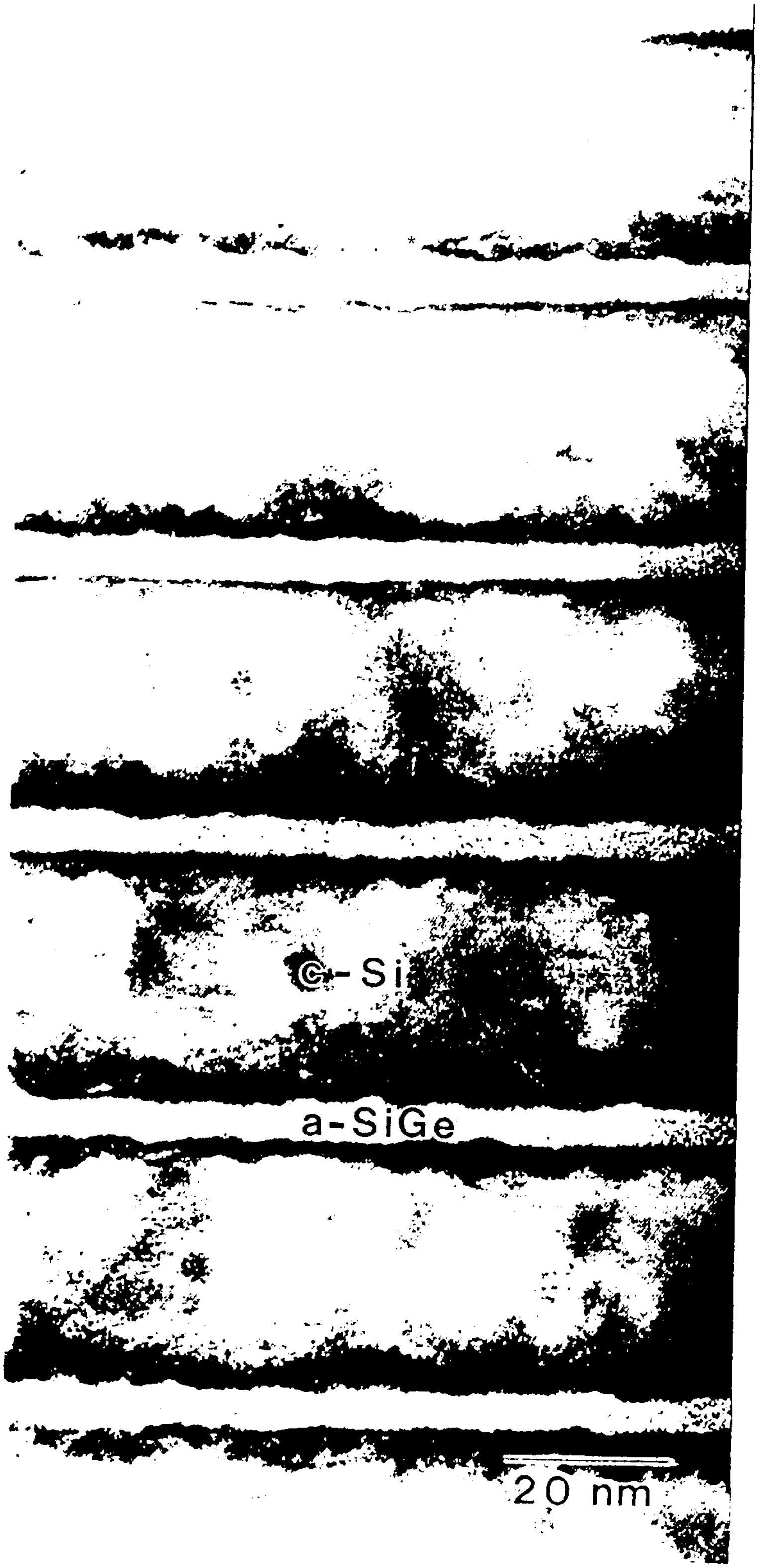
10A. Ksendzov, R.W. Fathauer, T. George, W.T. Pike, and R.P. Vasquez, unpublished,

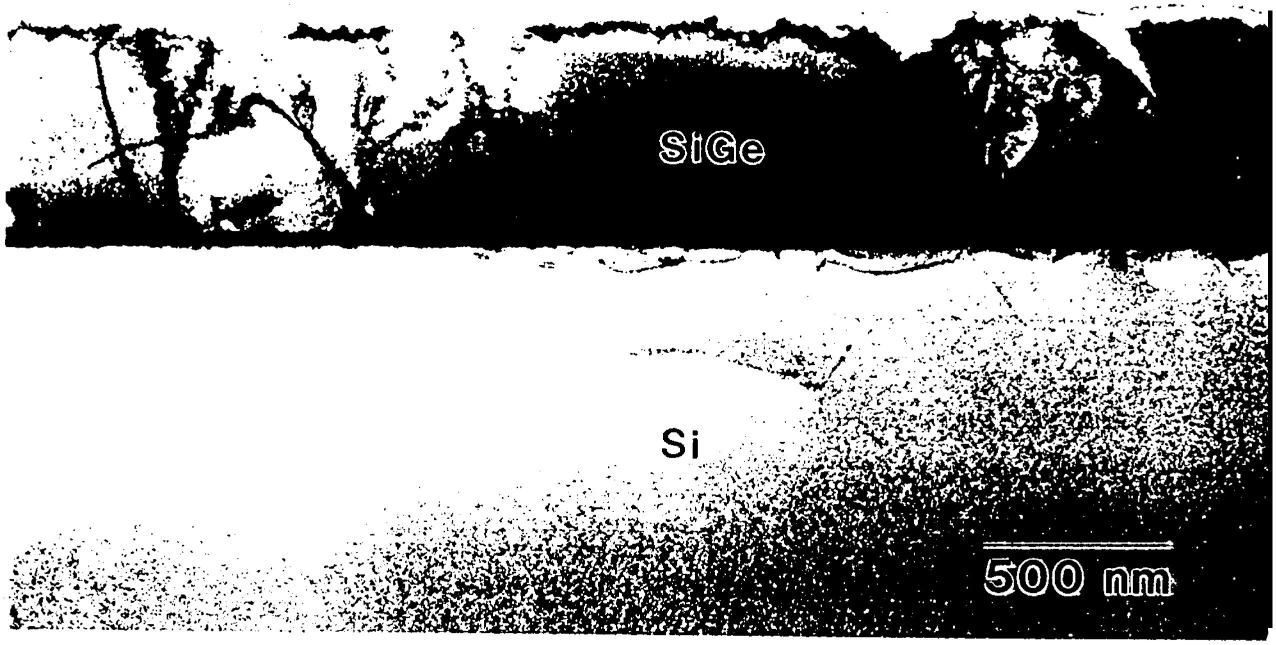
FIGURE CAPTIONS

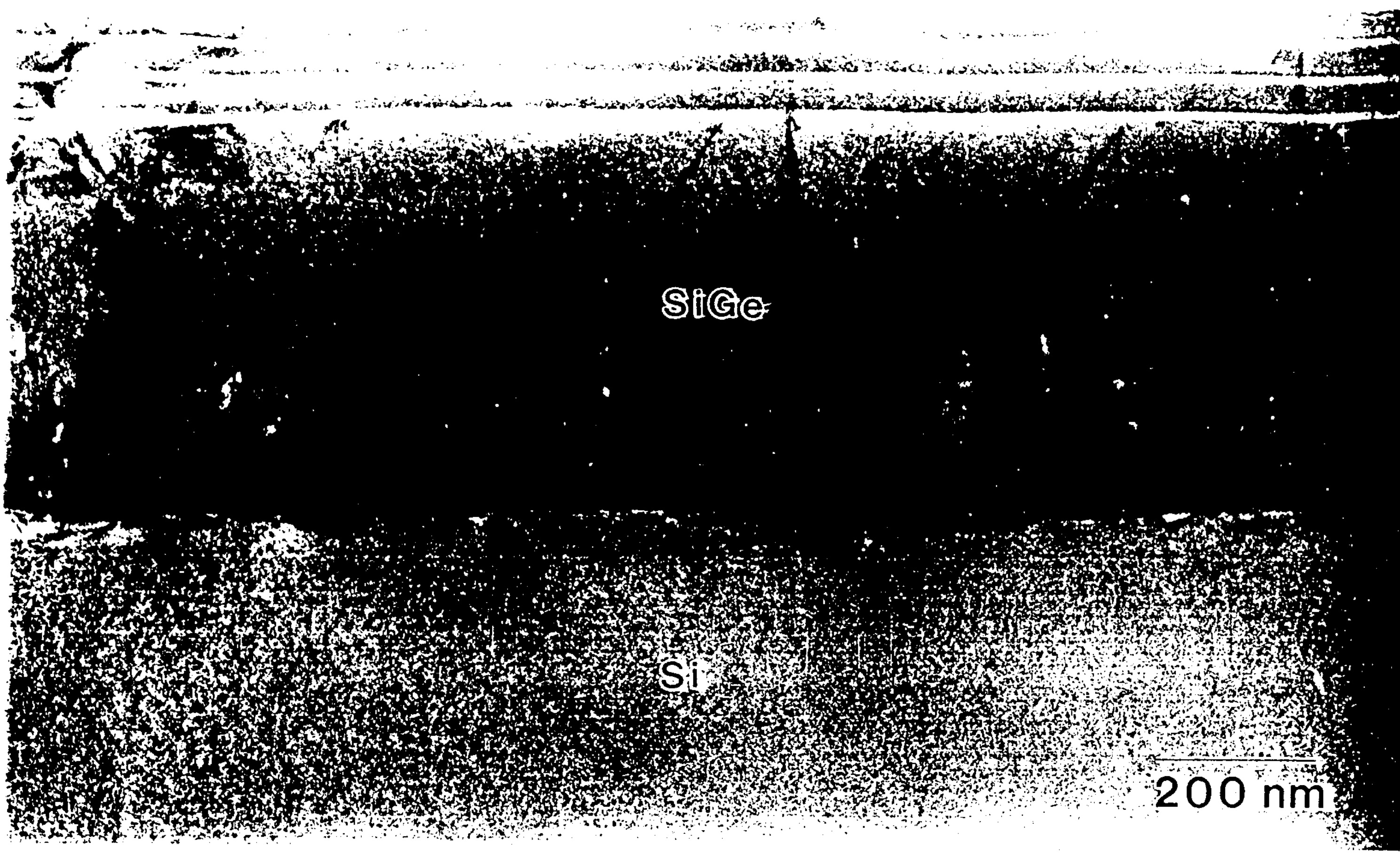
1. Cross-sectional TEM micrograph of a crystalline- Si/porous-amorphous-SiGe superlattice formed by stain etching of an MBE-grown superlattice consisting of alternating layers of Si (30 nm thick) and $Si_{.7}Ge_{.3}$ (5 nm thick). The darkening of the Si layers at the interfaces with the porous layers is a fringing effect in the TEM.

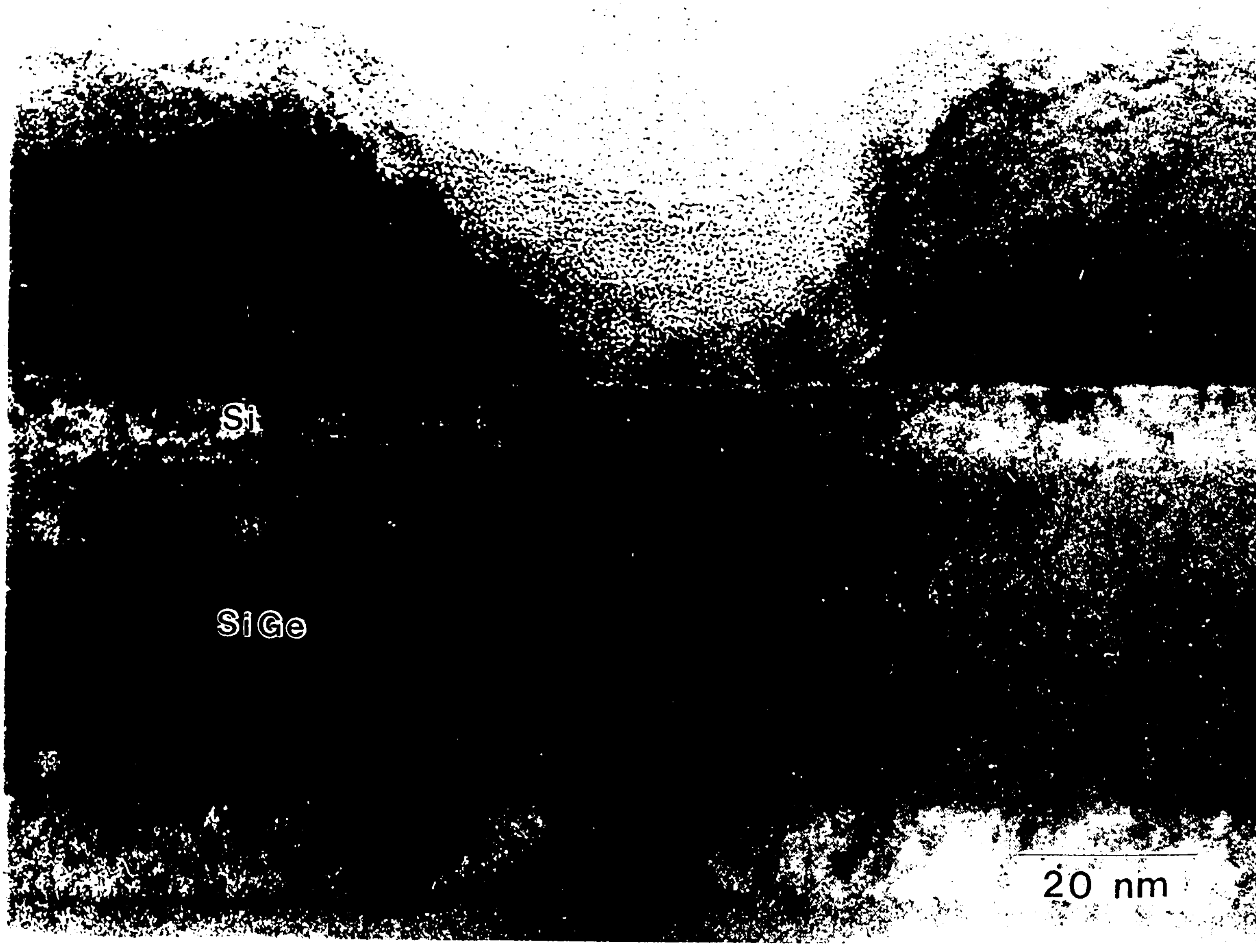
2. Cross-sectional TEM micrograph of a 0.75-μm-thick $Si_{.8}Ge_{.2}$ alloy layer grown above the critical thickness for the introduction of misfit dislocations and immersed in a stain solution. Porosification has occurred to a much greater depth along threading dislocations than in the layer as a whole.

3. Cross-sectional TEM micrographs of a strained-Si/relaxed-$Si_{.7}Ge_{.3}$ multilayer structure grown by MBE on a relaxed $Si_{.7}Ge_{.3}$ buffer layer, subjected to stain etching. Pore formation is enhanced along threading dislocations (as in Fig. 2), but stops abruptly at strained Si layers. The lower magnification image (a) shows the full epitaxial structure, while the lattice image (b) shows the abrupt termination of the porous region at the top Si layer.


c-Si
a-SiGe
20 nm


SiGe
Si
500 nm


SiGe
Si
200 nm


Si
SiGe
20 nm